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Description

This invention concerns fire-retardant compositions and a method of providing or enhancing fire-retardant properties of materials and compositions.

If alumina trihydrate is used as an additive to plastics materials, as a fire retardant, several difficulties emerge. Alumina trihydrate produces water, up to 30% of its weight, at temperatures of 200 degrees C. This water turns to steam, and blankets burning action. It follows therefore, that alumina trihydrate cannot be used in plastics materials which are processed at temperatures above 185 degrees C (to leave a safety margin). Such plastics materials include polypropylene and polyethylene.

Secondly, to be effective, levels of 60% by weight and even 64% by weight of alumina trihydrate have been used in urethane methacrylate and polyesters. Such high amounts of a filling make the resin very difficult to work.

Thirdly, alumina trihydrate is supplied in various grades priced according to their micron size. The cheapest is at 25 micron particle size, the dearest at about 10 micron. The larger particles are in plate form which makes them difficult to disperse in high concentrations, and that can also have an adverse effect on surface finish. The smaller particles are rounded during processing and disperse more easily but are more expensive by a factor of three compared to the larger particles.

Another popular fire retardant additive is antimony oxide. Antimony oxide works by combining with free halogen but is only partially effective, in that it improves existing fire retardant properties rather than making materials conform to rigorous tests. Antimony oxide is usually used in amounts of 3% by weight, although higher amounts may be used in some materials.

In copending European Application No. 88301024 (published as No. 0,278,711A) there are described fire-retardant moulded components having, as filling within a pre-formed outer skin, certain compositions comprising two or more frits melting progressively as the temperature rises under fire conditions.

According to the present invention there is provided a fire-retardant composition comprising a polymer or sodium silicate, characterised in that the composition further comprises two or more frits capable of melting progressively as the temperature rises under fire conditions, provided that when the said composition comprises a resin or sodium silicate together with ceramic fibres or powder the said frits melt at temperatures of at least 450 degrees C.

The frits under fire conditions will melt progressively to provide a fused protective layer. A preferred frit combination comprises a relatively low-melting frit e.g. that starts to melt at about 450 degrees C and a relatively high-melting frit that starts to melt at about 700 degrees C. The preferred weight ratio of low melt frit to high melt frit is in the range 1:9 to 1:1, especially 3:7. A typical selection of frits may be from those that melt at or about the following temperatures: 450 degrees C, 650 degrees C, 850 degrees C and 1000 degrees C. The frits used are preferably oven dried, water washed and ground prior to inclusion in the compositions of the invention.

In co-pending European Application No. 90121158 a divisional of the present application, there are described fire-retardant compositions comprising two or more frits melting progressively as the temperature rises under fire conditions, wherein one of the said frits is a relatively high-melting frit which is a devitrifying frit.

The inclusion of ceramic in fibre or powder form can be used to bind the melting frits and also to remain unchanged at temperatures above 1000 degrees C. Basalt fibre or chopped fibre or powder can also be used in place of or in addition to the ceramic material.

The compositions of the invention may also comprise one or more other fire retardant additives. For example an intumescent substance or substances may be included in the compositions of the invention, such as alumina trihydrate which releases most of its chemically combined water between 200 and 330 degrees C to dampen burning and reduce smoke emission, or hydrated magnesium calcium carbonate which releases its chemically combined water and carbon dioxide from 230 degrees C upwards. For some purposes hydrated magnesium calcium carbonate may be preferable to alumina trihydrate because it is less expensive to obtain in very finely divided form say of the order of 2 to 3μ particle size. A preferred composition of frits and intumescent substance or substances comprises from 15-50%, especially 20-30% by weight of frits and 85 to 50%, especially 80-70%, by weight intumescent substance(s). Another example of fire retardant additives may be antimony oxide usually used in combination with halogenated hydrocarbon, whereby halogen free radicals are produced that suppress burning.

The proportion of frits to ceramic or basalt in a preferred embodiment of the invention is about 7:3.

The compositions of the invention may be added to a variety of materials such as polymers, paints and sodium silicate. Suitable polymers include polyesters, phenolic resins, polyurethanes and other thermosetting resins and thermoplastics. If, however, alumina trihydrate is to be included in the additive composition, the composition cannot be used with materials processed at 200 degrees C

or above (and preferably not with materials processed at 185 degrees C or above).

In a phenolic resin, for example, the proportion of an additive composition of the invention comprising frits and ceramic or basalt to resin may be from 3:7 to 1:4.

The frits additive with intumescent substance, such as hydrated magnesium calcium carbonate or alumina trihydrate or a mixture thereof, may be added to dough moulding compounds, such as of the phenolic or polyester type to be used with glass reinforcement. Preferably the ration of frits to instumescent is about 1:4.

For addition to phenolic resin, a frits/intumescent substance mix ratio in the range of from 7:3 to 5:5 may be used, the preferred ratio of that mix to phenolic resin being in the range of 3:7 to 4:6.

The action of heat on a resin which contains an additive composition according to the invention has the following effect. The resin or plastics material burns and the frit in the first temperature band melts and combines with the char. The second frit then melts and so on. The substrate and burning material are encapsulated by the molten frits thus starving the fire of oxygen. The ceramic or basalt or both, if present, insulate and stiffen the molten mass to prevent excessive running. They also contribute greatly to stability at high temperatures.

Since the particle size of the frits and ceramic can be controlled they are suitable for use with alumina trihydrate in its coarse form. The particles fill the gaps between the alumina trihydrate plates to give a better finish. The plates of alumina trihydrate act as a suspension agent for the frits/ceramic mix.

The addition of mixes to sodium silicate has a beneficial effect, in that the frits tend to plasticise the sodium silicate under increasing temperature conditions; this counteracts the embrittlement and powdering of the sodium silicate normally encountered in these conditions. The inclusion of frits in an intumescent seal or paint formula would constitute an improvement.

It is preferred to use a mix of frits and intumescent substance, such as hydrated magnesium calcium carbonate or alumina trihydrate or a mixture thereof, say in the ratio of 3:7 to 1:1, preferably 4:6, with sodium silicate, and by varying the ratio of the frit mix to sodium silicate, materials suitable for different uses may be obtained. At a ratio about 1:1 the resultant mixture has a paint consistency, at a ratio of about 7:13 the mixture has adhesive properties and at a ratio of about 1:4 the mixture is in a gel form.

The frit composition of the invention may be used to make sealant say for around fire doors or windows. The preferred sealant will swell when heated and stop any gaps around say doors or windows.

For a sealant paste a frit combination containing intumescent with sodium silicate say in the ratio of 3:7 to 4:6, preferably 7:13 by weight may be used as a base to which is added a char agent, such as mica, ammonium polyphosphate and an inorganic gelling agent. The resultant paste is one which will harden in situ.

By using polyvinylacetate in place of the sodium silicate, a resilient sealant may be produced that will swell and harden when heated.

Another possible use of the additive composition of the invention is in the production of sheets or boards made by compression of chips of wood with a binder. Thus, the binder may be a composition comprising phenolic resin or sodium silicate solution containing ceramics, such as CARBORUNDUM (Registered Trade Mark), and frits according to the invention, preferably three frits having different melt temperatures.

A further use of the additive composition of the invention may be as an adhesive. The preferred adhesive will be based on sodium silicate solution containing a catalyst or phenolic resin and the composition of the invention. Such an adhesive may be used in circumstances where fire resistance is important.

For example, the adhesive may be used for bonding facing sheets, such as of melamine, to a base material, such as chipboard. Then, under fire conditions, the adhesive can provide a protective shield for the base material even when the facing sheet has been burnt off.

Another particular use is as an adhesive for attaching a brake lining to its carrier. Indeed brake linings may be made from the same composition, the ceramic material preferably being slag fibre and shot, such as produced as waste from power stations. The brake linings material may comprise additional strengthening components, such as carbon fibre or thermoplastics material e.g. KEVLAR (Registered Trade Mark).

Another example of using frits is in the construction of a laminate comprising an outer skin formed by heat and pressure where a glass cloth has been impregnated with a liquid settable resin, such as phenolic, containing a frit composition according to the invention together with a binding heat stable, fibre, such as ceramic mullite fibre, and optionally alumina trihydrate. The skins of impregnated cloth are placed on either side of a ceramic paper, combination basalt, ceramic and glass fibre paper, glass cloth treated with vermiculite or indeed any heat resistant barrier material. When this laminate is pressed under heat and with any number of interleaved sheets the settable resin migrates into the barrier material to produce a solid

sheet.

When flame is applied to the laminate the settable resin burns to protect the substrate, the barrier material providing stability.

The surface of the laminate may be covered with melamine sheet either plain or patterned or real wood veneer; when flame is applied, the frits/ceramic help to form a char and prevent spread of flame. This moulded laminate, flat or three dimensional, can then be adhered to a substrate, such as a door, using sodium silicate containing the same frits, ceramic fibre and optionally alumina trihydrate previously mentioned to make a high heat performance adhesive.

The substrate can be a rigidized sheet of ceramic fibre which is in turn adhered, with the adhesive described, to a heat resistant sound deadening core made from say basalt fibre or rockwool rigidized or non-rigidized. The construction may be repeated about the centre line.

For thirty minute rating the pressed laminate adhered and/or mechanically fixed to a basalt or rockwool core is sufficient. For sixty minutes rating the rigidized ceramic board may be introduced, and for extended times the ceramic board can be increased in thickness and a ceramic non-rigid blanket can be used instead of the rockwool/basalt core. For light weight constructions a phenolic foam core or a foam made from the adhesive mentioned can be used.

A foamed vermiculite clay can be included in the adhesive to produce a lightweight, highly insulating core. Alternatively, a core can be made by using woodchip as a filler to the adhesive to make a high heat resistance chipboard core to a door, building panel or partition.

This invention will now be further described by means of the following examples.

Example 1

A mix containing antimony oxide 3% by weight, one frit at a low temperature melt band at 10% by weight, one frit at a high temperature melt band (of approximately 1100 degrees C) at 60% by weight and ceramic at 27% by weight made up a casting or injection material which was suitable for use with a phenolic or sodium silicate binder as well as other materials including thermosets and thermoplastics.

Example 2

A mix contaning antimony oxide 3% by weight, one frit at a low temperature melt band at 7% by weight, one frit at a high temperature melt band (of approximately 1100 degrees C) at 45% by weight and alumina trihydrate at 45% by weight made a mix suitable for polyesters and other materials including thermosetting resins whose processing is not done above 185 degrees C.

Example 3

Dough moulding compounds for use with glass fibre reinforcement were prepared based on phenolic resin and on polyester resin. In both cases a powder mix of 20% by weight frits (low and high melting in a ratio of 3:7) and 80% by weight of hydrated magnesium calcium carbonate were added to the resin.

Claims

1. A fire-retardant composition comprising a polymer or sodium silicate, characterised in that the composition further comprises two or more frits capable of melting progressively as the temperature rises under fire conditions, provided that when the said composition comprises a resin or sodium silicate together with ceramic fibres or powder the said frits melt at temperatures of at least 450 degrees C.

2. A composition according to Claim 1 characterised in that the frits melt within the range from about 450 degrees C to about 1100 degrees C.

3. A composition according to Claim 2, characterised in that the composition comprises (i) a relatively low-melting frit that starts to melt at about 450 degrees C and (ii) a relatively high-melting frit that starts to melt at about 700 degrees C.

4. A composition according to any of the preceding claims characterised in that the weight ratio of low-melting frit to high-melting frit is in the range from 1:9 to 1:1.

5. A composition according to any of the preceding claims characterised in that the composition further comprises an intumescent substance.

6. A composition according to Claim 5, characterised in that the intumescent substance is alumina trihydrate or hydrated magnesium calcium carbonate.

7. A composition according to Claim 5 or Claim 6 characterised in that the proportion of frits is from 15% to 50% by weight of the total of frits and intumescent substance.

8. A composition according to any of the preceding claims characterised in that the composition further comprises ceramic fibres or powder.

9. A composition according to any of the preceding claims characterised in that the composition further comprises basalt fibres or powder.

10. A composition according to any of the preceding claims characterised in that the polymer is a phenolic or polyester resin.

11. A composition according to Claim 10 characterised in that the polymer is polyvinyl acetate.

12. A composition according to any of the preceding claims in the form of a paint composition.

13. A composition according to any of Claims 1 to 11 in the form of a sealant composition.

14. A composition according to any of Claims 1 to 11 in the form of an adhesive composition.

15. A composition according to any of Claims 1 to 11 in the form of a moulding composition.

16. A method of providing or enhancing fire-retardant properties of a material or composition, characterised by incorporation therein of two or more frits capable of melting progressively as the temperature rises in a fire situation, provided that when the said composition comprises a resin or sodium silicate together with ceramic fibres or powder the said frits melt at temperatures of at least 450 degrees C.

Patentansprüche

1. Feuerhemmende Masse, umfassend ein Polymer oder Natriumsilikat, dadurch gekennzeichnet, daß die Masse ferner zwei oder mehrere Fritten umfaßt, die bei ansteigender Temperatur unter Feuerbedingungen fortschreitend schmelzen können, vorausgesetzt, daß diese Fritten, wenn die Masse ein Harz oder Natriumsilikat zusammen mit Keramikfasern bzw. -pulver umfaßt, bei Temperaturen von mindestens 450 Grad C schmelzen.

2. Masse nach Anspruch 1, dadurch gekennzeichnet, daß die Fritten innerhalb des Bereichs zwischen ungefähr 450 Grad C und ungefähr 1100 Grad C schmelzen.

3. Masse nach Anspruch 2, dadurch gekennzeichnet, daß die Masse (i) eine relativ niedrigschmelzende Fritte, die bei ungefähr 450 Grad C zu schmelzen beginnt, und (ii) eine relativ hochschmelzende Fritte, die bei ungefähr 700 Grad C zu schmelzen beginnt, umfaßt.

4. Masse nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daS das Gewichtsverhältnis zwischen niedrig- und hochschmelzender Fritte im Bereich zwischen 1:9 und 1:1 liegt.

5. Masse nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Masse ferner einen intumeszierenden Stoff umfaßt.

6. Masse nach Anspruch 5, dadurch gekennzeichnet, daß der intumeszierende Stoff Aluminiumhydrat oder hydriertes Magnesiumcalciumcarbonat ist.

7. Masse nach Anspruch 5 oder Anspruch 6, dadurch gekennzeichnet, daß der Frittenanteil zwischen 15 und 50 Gewichtsprozent des Gesamtgewichts von Fritten und intumeszierendem Stoff beträgt.

8. Masse nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Masse ferner Keramikfasern bzw. -pulver umfaßt.

9. Masse nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Masse ferner Basaltfasern bzw. -pulver umfaßt.

10. Masse nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Polymer ein Phenol- bzw. Polyesterharz ist.

11. Masse nach Anspruch 10, dadurch gekennzeichnet, daß das Polymer Polyvinylacetat ist.

12. Masse nach einem der vorhergehenden Ansprüche in Form einer Farbenzusammensetzung.

13. Masse nach einem der Ansprüche 1 bis 11 in Form einer Dichtungsmasse.

14. Masse nach einem der Ansprüche 1 bis 11 in Form eines Klebemittels.

15. Masse nach einem der Ansprüche 1 bis 11 in Form einer Formmasse.

16. Verfahren zur Bereitstellung oder Verbesserung der feuerhemmenden Eigenschaften ei-

nes Materials bzw. einer Masse, gekennzeichnet durch die Beimengung hierzu von zwei oder mehreren Fritten, die bei ansteigender Temperatur unter Feuerbedingungen fortschreitend schmelzen können, vorausgesetzt, daß diese Fritten, wenn die Masse ein Harz oder Natriumsilikat zusammen mit Keramikfasern bzw. -pulver umfaßt, bei Temperaturen von mindestens 450 Grad C schmelzen.

Revendications

1. Composition ignifuge comprenant un polymère ou du silicate de sodium, caractérisée en ce que la composition comprend en outre deux frittes ou plus susceptibles de fondre progressivement au fur et à mesure que la température s'élève dans des conditions de feu, pourvu que lorsque ladite composition comprend une résine ou du silicate de sodium avec des fibres céramiques ou de la poudre céramique lesdites frittes fondent à des températures d'au moins 450 degrés C.

2. Composition selon la revendication 1, caractérisée en ce que les frittes fondent dans la gamme d'environ 450 degrés C à environ 1100 degrés C.

3. Composition selon la revendication 2, caractérisée en ce que la composition comprend (i) une fritte fondant à température relativement basse qui commence à fondre à environ 450 degrés C et (ii) une fritte fondant à température relativement élevée qui commence à fondre à environ 700 degrés C.

4. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que le rapport en poids de la fritte fondant à basse température à la fritte fondant à température élevée est dans la gamme allant de 1:9 à 1:1.

5. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que la composition comprend en outre une substance intumescente.

6. Composition selon la revendication 5, caractérisée en ce que la substance intumescente est du trihydrate d'alumine ou du carbonate de calcium et de magnésium hydraté.

7. Composition selon la revendication 5 ou la revendication 6, caractérisée en ce que la proportion de frittes est de 15% à 50% en poids du total de frittes et de substance intumescente.

8. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que la composition comprend en outre des fibres céramiques ou de la poudre céramique.

9. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que la composition comprend en outre de la poudre de basalte ou de la laine de basalte.

10. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que le polymère est une résine phénolique ou de polyester.

11. Composition selon la revendication 10, caractérisée en ce que le polymère est de l'acétate de polyvinyle.

12. Composition selon l'une quelconque des revendications précédentes, sous forme d'une composition de peinture.

13. Composition selon l'une quelconque des revendications 1 à 11, sous forme d'une composition de matériau d'étanchéité.

14. Composition selon l'une quelconque des revendications 1 à 11, sous forme d'une composition adhésive.

15. Composition selon l'une quelconque des revendications 1 à 11, sous forme d'un mélange à mouler.

16. Méthode pour prévoir ou rehausser des propriétés ignifuges d'une matière ou d'une composition, caractérisée par l'intégration dans celle-ci de deux frittes ou plus susceptibles de fondre progressivement au fur et à mesure que la température s'élève dans une situation de feu, pourvu que lorsque ladite composition comprend une résine ou du silicate de sodium avec des fibres céramiques ou de la poudre céramique lesdites frittes fondent à des températures d'au moins 450 degrés C.